

Sediment geochemistry in coastal maritime Antarctica (Admiralty Bay, King George Island): Evidence from rare earths and other elements

Isaac R. Santos^{a,*}, Déborah I.T. Fávaro^b,
Carlos E.G.R. Schaefer^c, Emmanoel V. Silva-Filho^a

^a Departamento de Geoquímica, Universidade Federal Fluminense, 24020-007, Niterói-RJ, Brazil

^b Laboratório de Análise por Ativação com Nêutrons (LAN-CRPq), IPEN/CNEN-SP, Av. Prof. Lineu Prestes 2242,
CEP:05508-000, São Paulo, Brazil

^c Departamento de Solos, Universidade Federal de Viçosa, 36570-000, Viçosa-MG, Brazil

Received 15 May 2007; received in revised form 10 September 2007; accepted 12 September 2007

Available online 20 September 2007

Abstract

We report the concentrations of 22 elements in short coastal sediment cores of Admiralty Bay (King George Island, Antarctica) determined by Neutron Activation Analysis. We focus the discussion on rare earth elements (REE) because their fractionation patterns in sediments relative to local sources may offer insights about weathering, transportation, deposition, and diagenetic processes. We found strong correlations between REE and Th, indicating detrital origin. Despite strong Eh gradients, the Th-normalized redox-sensitive elements (e.g., Eu, Ce, Fe, As, and others) showed little variability within the sedimentary environment. The exceptions were U (depleted in the upper few centimeters) and Br (enriched in the upper few centimeters). While U appears to be removed from seawater via uptake across the boundary of reducing sediments, the mechanisms driving Br accumulation are unclear, but perhaps related to increasing diatom production driven by regional warming. A comparison with published concentrations from rocks representing the regional eroding units showed that the characteristics of source rock could be recognized in the REE fractionation patterns in our sediments. These results imply no significant alteration during weathering and sediment transport in the coastal region of Admiralty Bay and the prevalence of strong periglacial erosion in ice-free areas of MARITIME Antarctica in spite of the relatively mild regional environmental setting (e.g., high moisture and high temperatures).

© 2007 Elsevier B.V. All rights reserved.

Keywords: Sediment; Antarctica; REE; Weathering; Coastal environment; Diagenesis; Heavy metal; NAA; Bromine

1. Introduction

Weathering, transportation, deposition and diagenesis are major stages in the sedimentary cycle. These

stages, along with human interference, may exert varied influence on the distribution and abundances of elements in sediments. The distribution and fractionation patterns of rare earth elements (REE) in sediments relative to those in local source rocks may be related to these factors. Geochemical characteristics, including REE abundances, of sediments may be useful for identifying sediment origin in relation to local rocks

* Corresponding author. Department of Oceanography, Florida State University, Tallahassee, Florida 32306-4320, USA.

E-mail address: santos@ocean.fsu.edu (I.R. Santos).

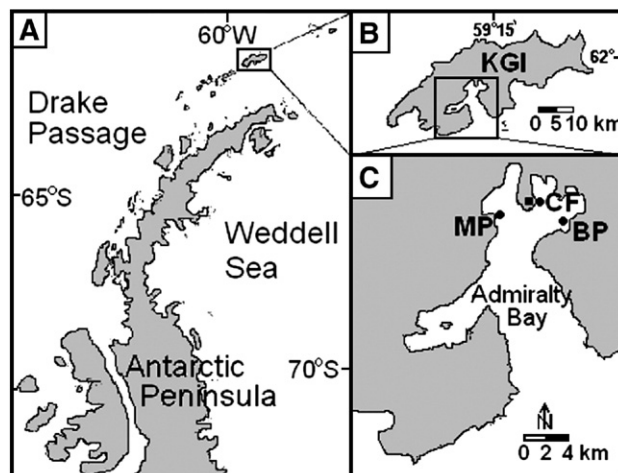


Fig. 1. Location of our sampling points in Admiralty Bay in relation to the Antarctic Peninsula and the King George Island (B). The square in (C) adjacent to the core CF depicts the location of Ferraz Station in Keller Peninsula.

(Chaudhuri and Cullers, 1979). Their chemical similarity renders REE less susceptible than other groups of elements to mutual fractionation in geochemical processes, and thus simplifies the interpretation of patterns observed in natural systems (Evensen et al., 1978). One may therefore assume that, if the concentration of REE in sediments is similar to local rocks, rock weathering and post-depositional processes, such as re-working and diagenesis, are not significant (Abanda and Hannigan, 2006).

In most parts of continental Antarctica, chemical weathering is not sufficiently important to cause major change in bulk composition of rocks, soils, and sediments. For example, a comparison between the mineralogy of bedrock with the mineralogy of sediments indicated that clay minerals must have originated by glacial erosion of the rocks of the South Shetland Islands (Jeong et al., 2004). In addition, the organic matter cycle may have negligible influence in soil and sediment geochemistry (Campbell and Claridge, 1987). However, in the maritime Antarctica, covering parts of the Antarctic Peninsula and the offshore islands, the climate is warmer, much greater quantities of free water are available, and bird guano may be very abundant locally (Myrcha et al., 1985; Bockheim and Ugolini, 1990; Schaefer et al., 2004; Michel et al., 2006). As a consequence, soil formation and chemical weathering occur to a greater extent than in other Antarctic areas (Blume et al., 1997; Beyer et al., 2000). Recent investigations showed that this process is important in small ice-free areas colonized by penguins, where soil organic matter accumulation and associated phosphatization are important (Michel et al., 2006; Simas et al.,

2006). Whether the regional extent and magnitude of this process are important enough to influence the geochemistry of coastal depositional environments remains to be answered.

Sediments provide a temporally integrated indication of the aquatic environment biogeochemical conditions and act as a major reservoir for reactive elements in the ocean. The fractionation patterns of REE between their source (rocks) and their sink (sediments) may provide information about the relative importance of chemical weathering processes (McLennan, 1989; Nath et al., 2000). Studies about sedimentation processes in coastal Antarctica may also be useful for understanding natural and/or anthropogenic, regional and/or global environmental changes (Gasparon et al., 2007). Atmospheric warming is believed to influence the distribution and amount of precipitation in Antarctica, and many studies have shown that the Antarctica Peninsula region is experiencing rapid climatic changes (Park et al., 1998; Simões et al., 1999; Simões et al., 2004; Thomas et al., 2004). If temperature, water availability, and ice cover are changed, the degree and rates of rock weathering and soil leaching are also altered. As a result, sedimentation processes in the coastal ocean may also be changed (Khim et al., 2001; Khim and Yoon, 2003).

The objectives of this paper are to characterize the vertical distribution of REE and other elements (U, As, Fe, Th, Br, Cr, Zn, and others) in coastal sediments of Admiralty Bay, maritime Antarctica, and to identify the main factors controlling their accumulation. By discussing vertical distribution patterns and comparing sediment concentrations with source rocks, we try to evaluate whether REE provide insights about sedimentological processes in coastal maritime Antarctica.

Table 1
Elemental concentrations in Admiralty Bay sediments

Core	Depth	<0.062	OM	As	Br	Ce	Co	Cr	Cs	Eu	Fe	Hf	La	Lu	Na	Nd	Rb	Sb	Sc	Sm	Tb	Th	U	Yb	Zn	
CF	0.5	97.5	8.8	150	1472	307	286	473	23.4	9.1	885	23.4	121	1.7	1463	300	743	3.7	527	34.9	5.9	19.2	4.7	11.7	1536	
	1.5	95.1	8.6	307	1315	321	289	521	22.8	9.4	902	24.7	131	2.7	1238	227	602	6.5	541	37.3	3.1	21.0	4.8	12.1	1514	
	2.5	95.0	8.0	174	1282	318	287	1015	24.5	9.1	876	23.7	128	2.2	1249	345	651	5.2	533	36.5	4.0	20.8	8.3	10.9	1429	
	3.5	96.2	7.9	274	1043	311	301	515	25.8	9.4	909	24.9	132	1.5	1202	269	871	8.5	549	38.0	4.7	20.2	8.6	12.1	1475	
	4.5	90.6	8.4	442	994	293	266	496	21.1	8.7	865	21.3	118	1.2	1076	264	745	5.7	490	34.0	4.2	19.3	10.0	11.4	1343	
	5.5	94.2	8.3	141	1005	305	291	478	25.1	9.7	869	24.2	130	1.7	1195	255	885	6.0	539	36.9	2.7	19.2	9.0	12.8	1379	
	6.5	94.3	8.0	196	912	305	282	520	22.1	8.6	839	23.1	121	0.0	1145	271	440	7.2	514	34.8	1.8	18.8	7.7	11.2	1424	
	7.5	88.4	7.7	262	938	330	293	500	25.3	8.1	898	24.0	127	4.0	1192	174	770	5.4	529	36.9	3.3	19.7	9.0	11.4	1746	
	8.5	96.0	7.6	336	920	329	280	519	25.4	8.8	899	25.2	133	2.3	1162	269	752	6.9	513	37.7	4.1	22.3	6.0	12.1	1687	
	9.5	79.3	9.4	260	879	327	291	565	24.5	9.5	892	24.4	135	3.9	1199	271	783	5.8	521	37.6	4.1	22.5	10.4	10.9	1776	
	11.0	94.9	9.2	171	925	319	307	536	26.0	9.2	880	24.4	128	2.4	1194	284	612	7.6	514	36.5	3.7	20.7	10.9	11.7	2065	
	13.0	87.5	7.0	108	772	324	297	489	22.2	9.2	852	24.4	133	2.1	1167	174	731	5.0	500	38.1	3.5	20.0	9.2	11.1	1622	
	15.0	81.0	6.1	215	686	314	274	568	16.8	8.9	835	23.0	135	2.4	1100	310	469	9.7	475	38.1	nd	18.4	8.4	10.2	1529	
	17.0	82.8	6.6	142	729	334	304	527	21.5	8.6	864	23.4	131	1.9	1141	188	803	5.2	498	36.1	3.8	18.8	8.5	9.9	1769	
	Mean		90.9	8.0	227	991	317	289	552	23.3	9.0	876	23.9	129	2.1	1195	257	704	6.3	517	36.7	3.8	20.1	8.3	11.4	1592
	Standard deviation		6.1	0.9	92	226	12	11	136	2.5	0.4	23	1.0	5	1.0	91	51	134	1.6	21	1.3	1.0	1.3	1.9	0.8	198
	MP	0.5	75.3	11.5	222	761	295	323	385	21.7	8.4	881	21.6	118	nd	1010	247	721	5.7	484	33.1	4.3	16.5	0.0	9.7	1604
1.5		58.1	4.7	230	625	313	333	433	22.4	7.9	910	23.4	128	nd	1004	211	762	7.9	488	34.8	nd	18.5	7.0	11.0	1759	
2.5		59.5	15.7	187	536	285	317	432	21.2	7.9	852	20.5	121	nd	924	159	664	7.1	466	34.2	4.5	18.4	5.5	9.8	761	
3.5		81.5	11.5	267	714	305	335	434	21.4	8.5	931	21.6	117	nd	864	111	652	6.7	508	34.0	nd	17.6	5.6	10.5	1328	
4.5		84.4	5.6	252	793	308	337	507	25.8	7.8	928	23.5	125	2.6	966	225	1118	7.0	505	34.6	4.4	18.3	7.4	11.3	1790	
5.5		89.0	5.4	252	855	299	340	384	27.5	8.6	819	22.9	121	1.5	953	214	1003	7.8	518	34.8	3.7	19.7	6.4	9.9	1760	
6.5		90.4	5.7	268	688	287	320	382	22.6	7.9	889	22.0	116	nd	940	86	858	6.0	487	32.7	nd	17.6	7.7	12.0	1747	
7.5		89.2	5.4	200	514	314	358	436	25.5	8.7	957	22.7	109	2.8	697	142	820	10.2	520	32.8	nd	20.2	7.5	9.8	2149	
8.5		89.4	5.9	176	472	288	317	364	27.1	7.6	882	21.4	101	nd	646	184	890	9.7	487	30.2	nd	16.1	7.5	9.5	1561	
9.5		75.4	4.8	216	485	300	353	353	26.9	8.0	942	23.5	126	nd	1049	177	1103	9.0	512	35.8	5.5	18.1	8.5	11.1	2180	
11.0		69.7	4.2	231	518	301	345	424	19.3	8.6	930	22.4	122	2.5	1070	186	1108	9.0	498	35.9	5.6	21.6	6.2	10.1	1690	
13.0		71.2	4.8	217	553	275	314	439	20.7	7.9	867	21.1	115	nd	1005	188	1050	8.8	462	33.5	nd	18.1	7.1	9.4	1067	
15.0		74.6	14.3	186	617	284	314	449	20.1	8.0	845	21.6	118	nd	1056	148	1111	7.0	454	32.8	5.2	17.1	5.0	9.4	1764	
17.0		75.2	16.3	201	607	305	313	400	28.2	8.3	882	22.6	120	nd	1127	192	837	8.1	484	34.3	nd	18.6	7.9	9.3	1534	
Mean			77.4	8.3	222	624	297	330	416	23.6	8.2	894	22.2	118	2.4	951	176	907	7.8	491	33.8	4.8	18.3	6.4	10.2	1621
Standard deviation			10.6	4.5	30	122	12	15	40	3.1	0.4	41	0.9	7	0.5	136	44	173	1.4	21	1.5	0.7	1.5	2.1	0.8	377
BP		0.5	91.7	10.0	73	1276	361	379	747	22.9	11.0	978	28.2	141	nd	1500	337	994	nd	542	41.1	1.5	21.2	nd	12.6	1381
	1.5	96.5	9.1	85	839	355	359	712	19.3	9.8	929	27.4	135	nd	1291	nd	472	nd	512	39.7	nd	23.5	nd	13.4	1453	
	2.5	95.8	8.5	63	773	352	356	681	20.5	9.6	910	27.5	131	nd	1301	96	588	nd	512	38.3	7.5	21.1	nd	10.2	1398	
	3.5	94.8	9.0	54	721	353	361	659	15.8	6.7	914	27.4	142	nd	1326	270	nd	nd	516	39.5	2.	22.0	nd	10.6	1331	
	4.5	96.9	8.9	48	638	338	376	757	16.4	9.7	939	28.3	110	nd	1305	334	825	nd	519	39.1	2.0	23.6	nd	11.5	1366	
	5.5	97.8	8.3	59	617	338	361	787	15.1	9.5	884	27.3	129	nd	1234	115	432	nd	501	37.3	4.7	20.7	nd	9.0	1404	
	6.5	98.3	8.6	52	611	330	344	695	15.6	9.5	866	24.3	124	nd	1224	147	nd	nd	481	37.1	1.8	21.0	nd	12.2	1368	
	7.5	94.7	6.3	58	719	349	357	828	13.9	9.8	887	24.6	134	1.8	1251	321	645	2.9	500	38.1	3.1	22.1	6.3	11.2	1286	
	8.5	95.0	8.2	49	585	355	388	844	19.4	10.1	945	26.3	143	2.2	1340	292	649	3.1	523	40.1	3.3	23.2	7.8	12.1	1376	
	9.5	91.9	7.4	56	608	349	372	836	20.6	10.2	935	25.2	140	1.6	1290	255	541	3.5	513	39.9	3.1	22.8	9.2	13.1	1454	
	11.0	97.3	8.1	53	665	344	359	731	14.9	9.9	906	25.2	136	1.4	1310	199	525	2.5	495	39.0	2.3	22.5	7.8	12.1	1283	
	13.0	97.3	8.2	69	532	318	357	827	18.9	9.7	900	24.2	137	nd	1291	279	426	4.0	490	38.9	4.7	22.7	11.4	10.8	1280	
	15.0	95.3	8.5	69	543	373	374	870	21.8	10.5	959	25.0	141	1.3	1315	249	386	3.6	515	40.5	3.6	21.5	12.5	11.1	1410	
	17.0	97.2	7.7	54	484	360	380	794	20.2	10.7	961	25.5	143	1.8	1284	225	661	2.8	513	40.8	3.8	21.4	6.6	12.0	1238	
	Mean		95.7	8.3	60	687	348	366	769	18.2	9.8	922	26.2	135	1.7	1304	240	595	3.2	509	39.2	3.4	22.1	8.8	11.6	1359
	Standard deviation		2.0	0.9	10	195	14	12	67	2.9	1.0	33	1.5	9	0.3	65	80	177	0.5	15	1.2	1.6	1.0	2.4	1.2	67

Values in nmol/g, except <0.062 and OM (%); and Fe and Na ($\mu\text{mol/g}$).

2. Material and methods

2.1. Site description

Admiralty Bay has an area of 131 km² and maximum depth of 530 m. This is the largest bay adjacent to the King George Island (KGI), which is located approximately at 63°S in the South Shetlands Islands (Fig. 1). These islands expose volcanic and plutonic rocks of Early Cretaceous to Early Miocene age with calc-alkaline affinity, which are related to the subduction of the SE-Pacific oceanic crust underneath the Antarctic continent. Mafic and intermediate volcanic rocks (i.e. basalts, basalt–andesites and andesites) are the dominant lithologies, whereas rhyolite and dacite are less abundant. Some areas contain sulphide minerals (Smellie et al., 1984; Groeneweg and Beunk, 1992; Machado et al., 1998; Machado et al., 2001; Schaefer et al., 2004; Machado et al., 2005; Santos et al., 2006; Simas et al., 2006).

The KGI is almost entirely ice-covered and the strong glacial influence is reflected by the fjord-like morphology of Admiralty Bay and the occurrence of moraine deposits. This region receives larger amounts of rainfall than the eastern and southern regions of the Antarctica Peninsula (Pichlmaier et al., 2004). Dissolution of the sulphide minerals may enhance rock weathering rates due to the formation of acid solutions (Åström, 2001; Borrego et al., 2005), so it is likely that chemical weathering occurs in the KGI. In Admiralty Bay, ¹⁴C-derived sedimentation rates varied between 0.36 mm/yr (before 1200 yr BP) and 2.27 mm/yr (since 1200 yr BP). Higher sedimentation rates in upper layers of sediments were attributed to a higher input of terrigenous material from meltwater streams probably as a response to regional warming (Yoon et al., 2000).

2.2. Sampling and analysis

Three short sediment cores (up to 25 cm long) (MP — Macchu Picchu; BP — Botanic Point; and, CF — Comandante Ferraz Station) were collected with a box-corer in the

coastal region of Admiralty Bay in January of 2004 during the XXII Brazilian Antarctic Expedition in a water depth of nearly 30 m (Fig. 1). Redox potential (Eh) and pH were measured immediately after core collection with portable electrodes in samples that were further used for biological analysis collected with the same box-corer. That is why Eh and pH data are available only for the first 10 cm of the cores. The cores used for geochemical analysis were sliced into one centimeter intervals (upper 10 cm) and into two centimeter intervals (below 10 cm) immediately after arriving in the laboratory of Ferraz Station. The samples were lyophilized (48 h at –46 °C and 133 × 10^{–3} mbar) and ground for trace element analysis. We did not wet-sieve the sample fraction used for metal analysis, but we did remove a few large grains (>2 mm) with a plastic forceps. Loss on ignition (hereafter assumed to represent the organic matter content — OM) was determined by burning previously dried sediment at 450 °C for 24 h, while the percentage of fine-grained sediment (<0.062 mm) was obtained after mechanical separation through wet sieving (Suguio, 1973).

Trace and REE were determined by Instrumental Neutron Activation Analysis technique (INAA) in the IEA-R1m nuclear research reactor at IPEN — Instituto de Pesquisas Energéticas e Nucleares, São Paulo, Brazil (Larizzatti et al., 2001). Approximately 150 mg of sediment (duplicate samples) were accurately weighed and sealed in pre-cleaned double polyethylene bags. Single and multielement synthetic standards were prepared by pipetting convenient aliquots of standard solutions (SPEX CERTIPREP) onto small sheets of Whatman n° 41 filter paper. Sediment samples, reference materials and synthetic standards were irradiated for 16 h, under a thermal neutron flux of 10¹² n cm^{–2} s^{–1}. Two series of counting were performed: the first after one week decay and the second after 15–20 days. The counting time was 2 h for each sample and reference materials, and half an hour for each synthetic standard. Gamma spectrometry was performed with a Canberra gamma X hyperpure Ge detector and associated electronics, with a resolution of 0.88 keV and 1.90 keV for ⁵⁷Co and ⁶⁰Co, respectively. Data analysis was made by

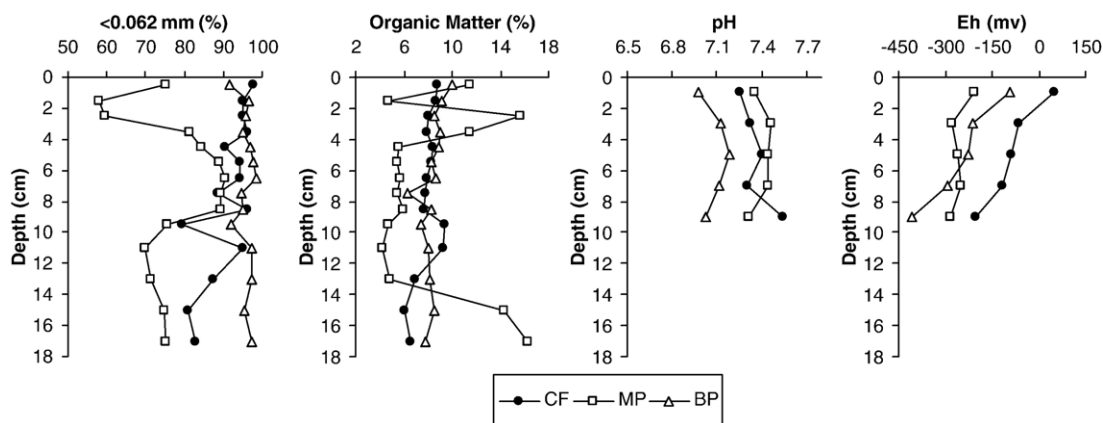


Fig. 2. Vertical distribution of grain size, organic matter (loss on ignition), pH, and Eh in coastal sediments of Admiralty bay.

Table 2
Pearson correlation coefficients for elements in Admiralty Bay sediments

	Fe	Sc	Th	As	Br	Co	Cr	Cs	Hf	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Na	Rb	Sb	U	Zn	>0.062	
Sc	0.44	1.00																						
Th	0.44	0.45	1.00																					
As	-0.30	-0.05	-0.49	1.00																				
Br	-0.13	0.61	0.06	0.28	1.00																			
Co	0.68	0.06	0.46	-0.70	-0.50	1.00																		
Cr	0.35	0.28	0.73	-0.67	0.05	0.48	1.00																	
Cs	-0.03	0.31	-0.41	0.55	0.28	-0.40	-0.53	1.00																
Hf	0.49	0.56	0.77	-0.62	0.17	0.52	0.66	-0.35	1.00															
La	0.30	0.36	0.62	-0.42	0.14	0.28	0.62	-0.29	0.61	1.00														
Ce	0.56	0.46	0.77	-0.66	0.03	0.58	0.77	-0.41	0.85	0.75	1.00													
Nd	0.09	0.41	0.42	-0.11	0.45	-0.08	0.45	-0.05	0.33	0.37	0.30	1.00												
Sm	0.45	0.46	0.83	-0.59	0.10	0.45	0.76	-0.42	0.83	0.87	0.87	0.45	1.00											
Eu	0.39	0.43	0.65	-0.51	0.18	0.39	0.69	-0.26	0.59	0.57	0.68	0.37	0.73	1.00										
Tb	-0.04	-0.20	-0.29	0.23	-0.08	-0.12	-0.28	0.23	-0.26	-0.16	-0.32	-0.42	-0.35	-0.26	1.00									
Yb	0.38	0.54	0.52	-0.16	0.40	0.11	0.37	-0.05	0.48	0.49	0.46	0.41	0.57	0.54	-0.49	1.00								
Lu	0.21	0.15	0.15	0.24	0.03	-0.10	-0.17	0.26	0.07	-0.01	0.02	-0.22	-0.03	-0.26	0.30	-0.17	1.00							
Na	0.25	0.43	0.68	-0.53	0.42	0.22	0.68	-0.38	0.74	0.73	0.70	0.52	0.83	0.65	-0.25	0.54	-0.18	1.00						
Rb	0.01	-0.09	-0.41	0.38	-0.02	-0.08	-0.57	0.46	-0.33	-0.44	-0.51	-0.17	-0.45	-0.48	0.18	-0.20	0.34	-0.38	1.00					
Sb	-0.21	-0.19	-0.54	0.56	-0.15	-0.32	-0.70	0.49	-0.55	-0.64	-0.67	-0.32	-0.62	-0.69	0.37	-0.53	0.20	-0.72	0.50	1.00				
U	0.12	0.15	0.29	-0.19	-0.13	0.05	0.35	0.08	0.31	0.36	0.34	0.28	0.39	0.35	-0.21	0.19	0.01	0.24	-0.35	-0.17	1.00			
Zn	0.07	0.17	-0.20	0.33	0.03	-0.14	-0.41	0.52	0.11	0.19	0.16	0.14	0.28	0.25	.24	0.06	0.54	0.30	0.37	0.39	0.13	1.00		
>0.062	0.19	0.56	0.54	-0.38	0.34	0.17	0.58	-0.19	0.61	0.32	0.56	0.30	0.50	0.55	-0.33	0.52	-0.44	0.52	-0.44	-0.49	0.26	-0.10	1.00	
OM	-0.13	-0.18	-0.09	-0.07	0.08	-0.07	0.00	0.00	-0.06	-0.02	-0.04	-0.03	-0.03	0.02	-0.01	-0.14	-0.05	0.15	-0.16	-0.14	-0.12	-0.35	-0.14	

Bold values are significant for $\alpha=0.01$ ($n=42$).

Critical coefficients are 0.30 for $\alpha=0.05$ and 0.39 for $\alpha=0.01$.

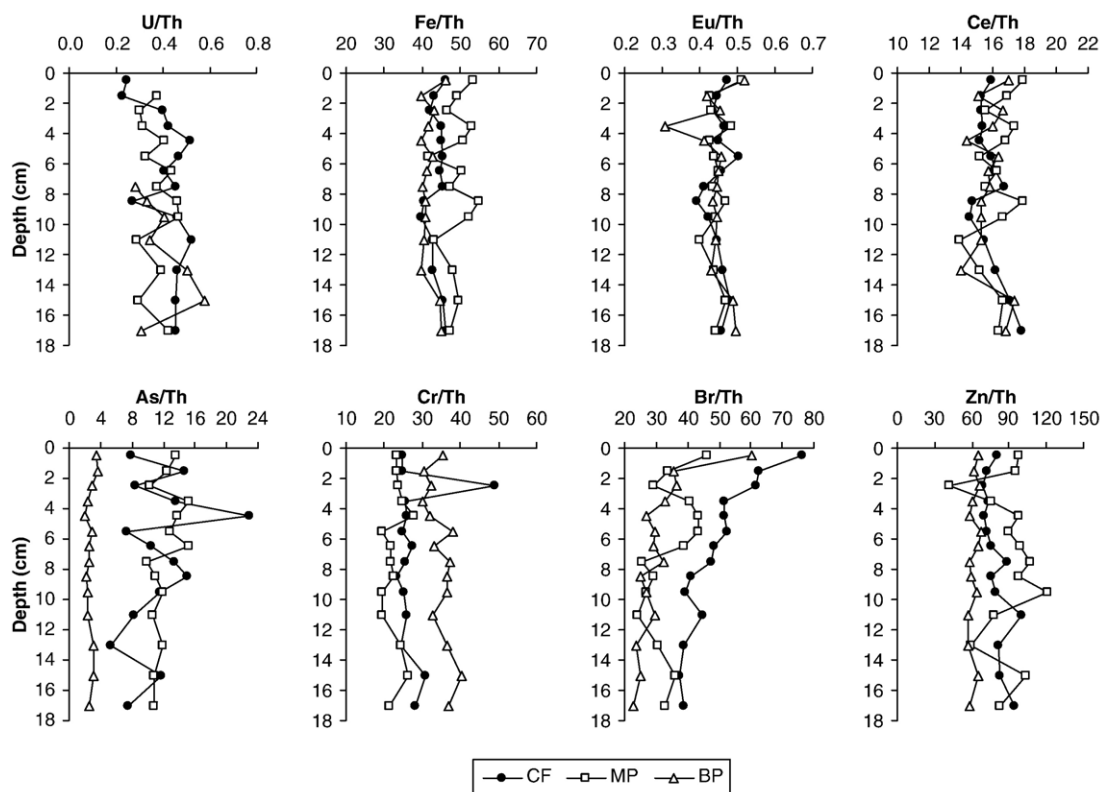


Fig. 3. Vertical distribution of selected Th-normalized elements (U, Fe, Eu, Ce, As, Cr, Br, and Zn) in coastal sediments of Admiralty bay.

VISPECT program to identify gamma-ray peaks and by ESPECTRO program to calculate concentrations. Both programs were developed at the LAN/CRPQ, IPEN.

The methodology was verified by measuring Buffalo River Sediment (NIST SRM 2704), Marine Sediment (PACS-2, National Research Council Canada) and BEN (Basalt-IWG-GIT) certified reference materials. Results of certified reference material analyses presented relative standard deviations lower than 5%. The agreement between the observed and the certified concentrations were better than 8%, indicating the precision of the analytical methodology. Additional details about the precision of our method and detection limits can be found elsewhere (Larizzatti et al., 2001; Wasserman et al., 2001; Oliveira et al., 2007). We report the concentrations of 22 elements (Table 1), but the discussion is focused on selected species (REE, U, Br, Th, and Fe).

3. Results and discussion

3.1. Major sediment characteristics

Grain size, organic matter, pH, and Eh are commonly the most important factors that control trace metals and REE accumulation in sediments. All three cores under study are characterized by approximately 8% of organic matter and a large fraction of muddy sediments (Table 1). The MP core had

the largest variability of fine-grained sediments and the lowest mean, perhaps as a result of short-term climatic fluctuations changing the amounts of local sediment supply and the rates of coastal primary production. Similar content and distribution of organic matter and grain size in the CF and BP cores (Fig. 1) indicate that the BP core could be used as a reference in order to assess the influence of Ferraz Station on chemistry of its adjacent sediments. In the CF core, <0.062 mm sediment content slightly decreased with depth, which may be related to some change of sedimentation processes near Ferraz Station. Indeed, recent investigations have shown significant retraction of Keller Peninsula glaciers at least since 1979, when the first detailed surveys were conducted (Simões et al., 2004). This probably enhances erosion processes on land, which may change land–ocean interactions and explain the higher mud content in the surface layers of the CF core. Another process that might explain the distinctive grain size distribution in the CF core is the human production of fine sediments derived from the grinding action of tracked vehicles (Gasparon and Burgess, 2001; Gasparon and Matschullat, 2006). However, further investigations are necessary to assess this hypothesis.

The sediments of Admiralty Bay had pH ranging from neutral to slightly alkaline (6.98 to 7.54), with a small depth-related variability (Fig. 2). On the other hand, we found a strong gradient of Eh within the sedimentary environment of Admiralty Bay (Fig. 2), which may influence the accumulation

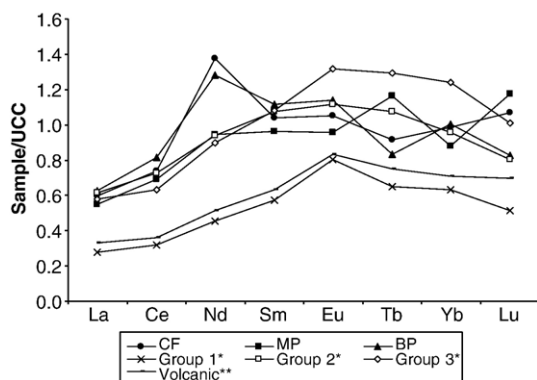


Fig. 4. Average concentrations of REE in sediments and rocks of the King George Island normalized by UCC concentrations. REE concentrations in rocks are from *Yeo et al. (2004) and **Machado et al. (2001).

patterns of redox-sensitive elements, such as U, Fe, Ce, and Eu. As expected, higher Eh values were found in the surface layers. The lowest Eh value (-407 mV) was observed in the 8–10 cm layer of BP core, indicating a strongly reducing environment. Although pH and Eh data are available only for the top 10 cm, it is reasonable to assume that below this layer the pH values are nearly constant and Eh values are either constant or more reducing. The steep near-surface Eh gradient indicates that microbial respiration is occurring in these sediments.

3.2. Vertical distribution of elements

Vertical distribution patterns of elements in coastal sediments may offer insights about how they respond to biogeochemical processes and to historical interferences in their cycle. By using a geochemical normalizer that is not influenced by diagenetic reactions and/or human activities, one can infer the occurrence of such processes in coastal sediments. Elements such as Al, Ti, Th, and Sc behave conservatively in the sedimentary environment and are usually not diagenetically active. In this paper we considered using Sc and/or Th as a geochemical normalizer, taking into account that both elements are reliable indicators of the contribution of terrestrial materials and are relatively immobile in aqueous solutions (Yang et al., 2004). We consider Th the preferred geochemical normalizer because it has the strongest correlations with most elements (Table 2). We should point out, however, that both Fe and Sc would lead to a similar interpretation because Fe, Sc, and Th are correlated to each other.

Pearson correlation coefficients (Table 2) were determined to examine the relationships among elements, which may give insights into the major factors controlling their accumulation. For a few elements (e.g., Lu, Tb, and U), this analysis is hampered by the fact that we could not determine their concentrations in all the samples (Table 1). Except for Tb and Lu, probably for the above reason, REE were strongly correlated with Th indicating their detrital origin. It can be

seen in Fig. 3 and Table 1 that, in spite of large redox potential gradients (Fig. 2), there is little variability in the vertical distribution of Th-normalized elemental concentrations. Relative standard deviations for elements within a certain core ranged from 3% to 47%, with most of them below 15%. These results imply that most elements are associated with the detrital phase and therefore early diagenesis is unlikely to occur in this setting. Elements such as Eu, Ce, Fe, As, and U are diagenetically active, so if diagenesis is occurring one might expect to see concentration variability along a redox potential gradient. For example, Ce^{+3} is oxidized to Ce^{+4} in oxygenated environments and the Ce^{+4} tends to be more rapidly removed by particle scavenging than the other REE in the +3 oxidation state (Nozaki et al., 2000). As a consequence, fractionation of Ce relative to other REE is expected to occur where strong redox gradients occur if Ce is not present mostly in the detrital phase.

The inference that the influence of diagenetic processes is minimal in our cores is supported by recent studies showing that sulphur within the sediment has not originated from in situ pyrite formation, but rather from the detrital supply of sand-sized quartz–pyrite rocks widely distributed in the KGI (Khim and Yoon, 2003). This may be explained not only by the fact that most elements seem not to be labile, but also by the regional environmental characteristics. Many studies have demonstrated that diagenesis can significantly mobilize REE, especially in organic-rich sediments (Lev and Filer, 2004; Abanda and Hannigan, 2006). In Admiralty Bay, the low temperatures and the relative low organic matter content do not favor diagenetic reactions. More importantly, proximity to the shore and high melt water supply during summer favor rapid sediment accumulation (Yoon et al., 2000; Figueira et al., 2005). Sedimentation rates derived from ^{137}Cs and ^{210}Pb in

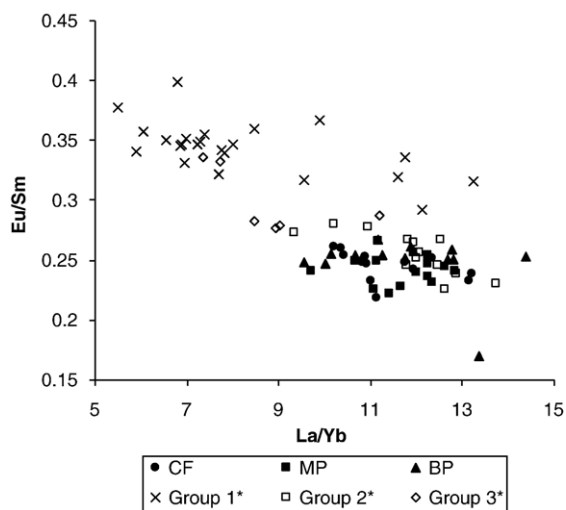


Fig. 5. Pair diagram between Eu/Sm and La/Yb for sediments and rocks of the King George Island. *REE concentrations in rocks are from Yeo et al. (2004).

Admiralty Bay in the last ~100 years were 3.5 mm/yr (Figueira et al., 2005), so the bottom of our cores is only about 52 years old. Apparently, such a fast accumulation rate probably has not provided sufficient time for chemical reactions to take place in our sediments.

Uranium was one of the few elements with a noticeable vertical trend (Fig. 3). U/Th ratios in the CF core were consistently lower in the upper layers, approaching zero in BP and MP cores. Its concentrations in reducing Admiralty Bay sediments may reach 13 nmol/g (overall average 8), while in local rocks it is lower than 4 nmol/g (Yeo et al., 2004). The main factors controlling U accumulation in sediments are adsorption onto Fe oxides and precipitation under reducing conditions (Swarzenski and Baskaran, 2006). Uranium may be mobilized as U^{+6} in oxic conditions and precipitated as U^{+4} in reducing environments due to anaerobic microbially-mediated processes. This process may occur relatively fast (hours) and explain U depletion in surface layers in many ocean sediments (Barnes and Cochran, 1990; Barnes and Cochran, 1993; Windom et al., 2000). In addition, U may be removed from seawater via uptake across the boundary of reducing sediments controlled by the oxygen penetration depth (Mangini et al., 2001; Dunk et al., 2002; McManus et al., 2005). Hence, because the U distribution pattern is not related to the Fe profile (Table 2) and because it is enriched in the sediments relative to local rocks, we suggest that it is derived from seawater and is controlled rather by oxygen contents in pore water. In other words, the redox-controlled precipitation appears to be more important than Fe-related diagenesis in Admiralty Bay sediments.

The other element with a clear vertical trend was Br, which was enriched in the upper layers of the three cores under investigation (Fig. 3). The distinctiveness of such profiles and the lack of correlations (Table 2) between Br and natural variables (e.g., Fe, grain size, organic matter) that might explain its distribution indicate a unique source for Br (the correlation between Br and Sc shown in Table 2 is clearly an artifact caused by the Br outliers). While its vertical distribution pattern is typical of contaminated sediments, it is unlikely that local anthropogenic inputs would change exclusively Br accumulation. If contamination sources, such as petroleum, sewage, and paints (Santos et al., 2005), are regionally important, one might expect other metals, such as As, Zn, Cr, and Co, to be enriched near the surface as well, which is not the case (Fig. 3).

Because dissolved Br is relatively high in seawater, it may be just precipitating in the upper few centimeters of our cores. Alternatively, global atmospheric deposition of brominated methanes largely used as a fumigant during the last few decades (Goodwin et al., 1997) might be a reason behind Br enrichment in our sediments. A third and perhaps more reasonable hypothesis would be the association of Br fluxes with increasing diatom production in maritime Antarctica. Bromine is highly enriched in the frustules of many diatom species, serving as a paleo-productivity proxy (Cota and Sturges, 1997; Kerfoot et al., 1999; Phedorin et al., 2000). Because of the fast regional warming and glacier retreat

observed around the KGI during the last few decades (Park et al., 1998; Simões et al., 1999; Simões et al., 2004), we hypothesize that Br accumulation in sediments may be reflecting higher primary production rates in Admiralty Bay supposedly driven by higher temperatures and higher melt-water (and nutrient) inputs. However, in order to accurately reveal Br accumulation driving mechanisms, it would be necessary to conduct additional experiments.

3.3. Comparison with local rocks

Comparisons between elemental concentrations in rocks and sediments may give insights into sediment source and weathering processes in Antarctica. The KGI can be divided in three tectonic blocks separated by strike-slip faults: Fildes Block, Barton Horst, and Warszawa Block (Birkenmajer et al., 1990; Birkenmajer, 2001). Data on REE in rocks of the KGI are available for the Fildes Peninsula, part of the Fildes Block (Machado et al., 2001; Machado et al., 2005), and for the Barton Peninsula, part of the Barton Horst (Lee et al., 2004; Yeo et al., 2004). Because our sediment samples were collected in an area adjacent to rocks of the Barton Horst, the dataset presented by Yeo et al. (2004) is the best one for the interpretation of REE fractionation patterns in sediments. Yeo et al. (2004) divided their studied volcanic rocks into three groups. Group 1 rocks showed relatively mafic compositions (basalts to basaltic andesites) and the lowest concentrations of trace and REE. Group 2 rocks are predominant in the KGI, and show intermediate compositions (basaltic andesites to andesites) with significantly higher P_2O_5 , K_2O , and SiO_2 and lower MgO , CaO , and Al_2O_3 contents than the Group 1 rocks. Additionally, Group 2 rocks contain smaller amounts of HREE, and thus have steeper chondrite-normalized LREE/HREE ratios. Group 3 rocks occur as intermediate dikes along restricted sectors of the KGI, generally with similar compositions to the Group 2 rocks. These differences among volcanic rocks reflect the complexity of parental magma and may influence sediment geochemistry.

The average concentrations of REE in sediments and rocks of the KGI normalized to concentrations in the Upper Continental Crust (Wedepohl, 1995) are shown in Fig. 4. We choose the UCC concentrations rather than other normalizers, such as NASC and chondrites, because REE fractionation in Admiralty Bay sediments is more discernible when standardized to UCC. UCC-normalized REE in sediments have a pattern similar to local rocks and, thus, appear to be primarily influenced by mechanical weathering of Group 2 rocks of Yeo et al. (2004). The lack of Ce and Eu anomalies in Fig. 4 also suggests that redox processes have not played a significant role in modifying the distribution of REE in these sediments. The similarity between Group 2 rocks and sediment REE concentrations are also depicted on the scatter plot between selected REE ratios (Fig. 5).

Admiralty Bay sediments exhibited a small enrichment of Heavy REE (HREE) and middle REE (MREE) in comparison with light REE (LREE) (Fig. 4). The effect of weathering on the fractionation of REE is commonly associated with the

preferential enrichment of LREE over the HREE in different soil and sediment horizons (Chaudhuri and Cullers, 1979; Condie et al., 1995), which appears not to be the case in Admiralty Bay. Differences between REE distributions in the source material and in the sink have been explained as a combination of factors, such as (1) the occurrence of additional, unknown sediment sources, (2) hydraulic sorting of minerals during deposition, and (3) diagenetic remobilization (Condie et al., 1995; Nath et al., 2000; Caccia and Millero, 2007). Taking into account that the dominant rocks from the KGI (Group 2 rocks) and adjacent coastal sediments have virtually the same REE distribution pattern, we can infer that negligible REE fractionation took place during weathering and transportation. This implies that the factors listed above and chemical weathering are not important enough to change REE concentrations in coastal sediments from Admiralty Bay.

This observation may seem contradictory to recent suggestions that chemical weathering is important in some coastal ice-free areas of Antarctica (Blume et al., 1997; Beyer et al., 2000; Blume et al., 2004), but it may be reconciled if we consider the spatial scale covered by subaerial soil surveys in relation to the spatial scale represented by our sediment observations. On the KGI, chemical weathering is considered an active process in areas rich in penguin guano and sulphides (Michel et al., 2006; Simas et al., 2006). Though important sites of chemical reactions, these areas cover a small percentage of the KGI ice-free areas (Schaefer et al., 2004). Because sediment composition represents whole basin processes, we suggest that the much larger spatial magnitude of physical weathering masks the influence of the local, smaller scale chemical weathering. Therefore, Admiralty Bay sediments appear to be originated predominantly from the breakdown of local bedrocks.

4. Conclusions

We reported results of Neutron Activation Analysis of coastal sediments from Admiralty Bay, maritime Antarctica. We found strong redox potential gradients, little vertical variability for most elements, and high correlations between Th and REE. The concentrations of rare earths and other elements are comparable to the dominant local rocks. These results imply that post-depositional processes have little influence on the geochemistry of the elements investigated here and that local bedrocks are the main source of sediments. The exceptions were U, which appeared to be controlled by redox-controlled precipitation from seawater, and Br, which has an indeterminate source (perhaps increasing diatom production). Our observations also implied the prevalence of strong periglacial erosion in ice-free areas of Maritime Antarctica in spite of the regional environmental setting (e.g., widespread sulphide mineral occurrence, high moisture, and relatively high

temperatures). Hence, physical weathering is likely to be regionally much more important than chemical weathering on the King George Island.

Acknowledgements

Sediment samples were collected with the Mini-Box Corer designed by the GEAMB group (Dr. Lucia Campos). We thank G Cavallaro for helping with laboratory work and John Winchester for reviewing the manuscript. Sampling collection was supported by the Brazilian Antarctic Program and the National Research Council (CNPq). IR Santos is currently supported by a CAPES/Fulbright fellowship at Florida State University.

References

- Abanda, P.A., Hannigan, H.E., 2006. Effect of diagenesis on trace element partitioning in shales. *Chemical Geology* 230 (1–2), 42–59.
- Åström, M., 2001. Abundance and fractionation patterns of rare earth elements in streams affected by acid sulphate soils. *Chemical Geology* 175, 249–258.
- Barnes, C.E., Cochran, J.K., 1990. Uranium removal in oceanic sediments and the oceanic U balance. *Earth and Planetary Science Letters* 97 (1–2), 94–101.
- Barnes, C.E., Cochran, J.K., 1993. Uranium geochemistry in estuarine sediments: controls on removal and release processes. *Geochimica et Cosmochimica Acta* 57 (3), 555–569.
- Beyer, L., Pingpank, K., Wriedt, G., Bölker, M., 2000. Soil formation in coastal continental Antarctica (Wilkes Land). *Geoderma* 95, 283–304.
- Birkenmajer, K., 2001. Mesozoic and Cenozoic stratigraphic units in parts of South Shetlands Islands and northern Antarctic Peninsula. *Studia Geologica Polonica* 118, 1–188.
- Birkenmajer, K., Guterch, A., Grad, M., Janik, T., Perchuc, E., 1990. Lithospheric transect Antarctic Peninsula–South Shetland Islands, West Antarctica. *Polish Polar Research* 11, 241–258.
- Blume, H.P., Beyer, L., Bolter, M., Erlenheuser, H., Kalk, E., Kneesch, S., Pfisterer, U., Schneider, D., 1997. Pedogenic zonation in soils of Southern circumpolar region. *Advances in GeoEcology* 30, 69–90.
- Blume, H.P., Chen, J., Kalk, E., Kuhn, D., 2004. Mineralogy and weathering of Antarctic cryosols. In: Kimble, J. (Ed.), *Cryosols-Permafrost Affected Soils*. Springer-Verlag, Berlin, pp. 415–426.
- Bockheim, J.G., Ugolini, F.C., 1990. A review of pedogenic zonation in well-drained soils of the southern circumpolar region. *Quaternary Research* 34 (1), 47–66.
- Borrego, J., Lopez-Gonzalez, N., Carro, B., Lozano-Soria, O., 2005. Geochemistry of rare-earth elements in Holocene sediments of an acidic estuary: environmental markers (Tinto River Estuary, South-Western Spain). *Journal of Geochemical Exploration* 86 (3), 119–129.
- Caccia, V.G., Millero, F.J., 2007. Distribution of yttrium and rare earths in Florida Bay sediments. *Marine Chemistry* 104, 171–185.
- Campbell, I.B., Claridge, G.G.C., 1987. Antarctica: soils, weathering processes and environment. *Developments in Soil Science* 16. Elsevier, Amsterdam. 368 pp.
- Chaudhuri, S., Cullers, R.L., 1979. The distribution of rare-earth elements in deeply buried Gulf coast sediments. *Chemical Geology* 24, 327–338.

- Condie, K.C., Dengate, J., Cullers, R.L., 1995. Behavior of rare earth elements in a paleoweathering profile on granodiorite in the Front Range, Colorado, USA. *Geochimica et Cosmochimica Acta* 59 (2), 279–294.
- Cota, G.F., Sturges, W.T., 1997. Biogenic bromine production in the Arctic. *Marine Chemistry* 56 (3–4), 181–192.
- Dunk, R.M., Mills, R.A., Jenkins, W.J., 2002. A reevaluation of the oceanic uranium budget for the Holocene. *Chemical Geology* 190 (1–4), 45–67.
- Evensen, N.M., Hamilton, P.J., O'Mions, R.K., 1978. Rare-earth abundances in chondritic meteorites. *Geochimica et Cosmochimica Acta* 42, 1199–1212.
- Figueira, R.C.L., Martins, C.C., Montone, R.C., Figueiredo, A.M.G., Tessler, M.G., Mahiquer, M.M., Cunha, I.I.L., 2005. Pb-210, Ra-226 and Cs-137 Levels and Sedimentation Rate in Admiralty Bay, Antarctic Peninsula. 1st International Nuclear Chemistry Congress, Kusadasi, pp. 289–290.
- Gasparon, M., Burgess, J.S., 2001. Human impacts in Antarctica: trace-element geochemistry of freshwater lakes in the Larsemann Hills, East Antarctica. *Environmental Geology* 39 (9), 963–976.
- Gasparon, M., Ehrler, K., Matschullat, J., Melles, M., 2007. Temporal and spatial variability of geochemical backgrounds in the Windmill Islands, East Antarctica: implications for climatic changes and human impacts. *Applied Geochemistry* 22 (5), 888–905.
- Gasparon, M., Matschullat, J., 2006. Geogenic sources and sinks of trace metals in the Larsemann Hills, East Antarctica: natural processes and human impact. *Applied Geochemistry* 21 (2), 318–334.
- Goodwin, K.D., North, W.J., Lidstrom, M.E., 1997. Production of bromoform and dibromomethane by giant kelp: factors affecting release and comparison to anthropogenic bromine sources. *Limnology and Oceanography* 42, 1725–1734.
- Groeneweg, W.J., Beunk, F.F., 1992. The petrography and geochemistry of the King George Island supergroup and Admiralty Bay group volcanics, South Shetland Islands. In: López-Martínez, J. (Ed.), *Geología de la Antártida Occidental. III Congreso Geológico de España y VIII Congreso Latinoamericano de Geología*, Salamanca, pp. 46–60.
- Jeong, G.Y., Yoon, H.I., Lee, S.Y., 2004. Chemistry and microstructures of clay particles in smectite-rich shelf sediments, South Shetland Islands, Antarctica. *Marine Geology* 209 (1–4), 19–30.
- Kerfoot, W.C., Robbins, J.A., Weider, L.J., 1999. A new approach to historical reconstruction: combining descriptive and experimental paleolimnology. *Limnology and Oceanography* 44 (5), 1232–1247.
- Khim, B.K., Hoon, H., Kim, Y., Shin, I.C., 2001. Late Holocene stable isotope chronology and meltwater discharge event in Maxwell and Admiralty bays, King George Island, Antarctica. *Antarctic Science* 13 (2), 167–173.
- Khim, B.K., Yoon, H.I., 2003. Postglacial marine environmental changes in Maxwell Bay, King George Island, West Antarctica. *Polar Research* 22 (2), 341–353.
- Larizzatti, F.E., Fávoro, D.I.T., Moreira, S.R.D., Mazzilli, B.P., Piovano, E.L., 2001. Multielemental determination by Instrumental Neutron Activation Analysis and recent sedimentation rates using ^{210}Pb dating method at Laguna del Plata, Cordoba, Argentina. *Journal of Radioanalytical and Nuclear Chemistry* 249 (1), 263–268.
- Lee, Y.L., Lim, H.S., Yoon, H.I., 2004. Geochemistry of soils of King George Island, South Shetland Islands, West Antarctica: implications for pedogenesis in cold polar regions. *Geochimica et Cosmochimica Acta* 68 (21), 4319–4333.
- Lev, S.M., Filer, J.K., 2004. Assessing the impact of black shale processes on REE and the U–Pb isotope system in the southern Appalachian Basin. *Chemical Geology* 206 (3–4), 393–406.
- Machado, A., Chemale Jr., F., Lima, E.F., Figueiredo, A.M.G., 1998. *Petrologia das rochas vulcânicas da Península Fildes, Ilha Rei George, Antártica. Pesquisas em Geociências* 25 (1), 35–42.
- Machado, A., Lima, E.F., Chemale Jr., F., Liz, J.D., Ávila, J.N., 2001. *Química mineral de rochas vulcânicas da Península Fildes (Ilha Rei George), Antártica. Revista Brasileira de Geociências* 31 (3), 299–306.
- Machado, A., Lima, E.F., Chemale Jr., F., Morata, D., Oteiza, O., Almeida, D.P.M., Figueiredo, A.M.G., Alexandre, F.M., Urrutia, J.L., 2005. Geochemistry constraints of Mesozoic–Cenozoic calc-alkaline magmatism in the South Shetland Arc, Antarctica. *Journal of South American Earth Sciences* 18 (3), 407–425.
- Mangini, A., Jung, M., Laukenmann, S., 2001. What do we learn from peaks of uranium and of manganese in deep sea sediments? *Marine Geology* 177 (1–2), 63–78.
- McLennan, S.M., 1989. Rare earth elements in sedimentary rocks: influence of provenance and sedimentary processes. *Reviews in Mineralogy and Geochemistry* 21, 169–200.
- McManus, J., Berelson, W.M., Klinkhammer, G.P., Hammond, D.E., Holm, C., 2005. Authigenic uranium: relationship to oxygen penetration depth and organic carbon rain. *Geochimica et Cosmochimica Acta* 69 (1), 95–108.
- Michel, R.F.M., Schaefer, C.E., Dias, L.E., Simas, F.B., Benites, V.M., Mendonça, E.S., 2006. Ormithogenic gelsols (cryosols) from maritime Antarctica: pedogenesis, vegetation, and carbon studies. *Soil Science Society of America Journal* 70, 1370–1376.
- Myrcha, A., Pietr, S.J., Tatur, A., 1985. The role of Pygoscelid penguin rookeries in nutrient cycles at Admiralty Bay, King George Island. In: Siegfried, W.R., Condy, P.R. (Eds.), *Antarctic Nutrient Cycles and Food Webs*. Springer-Verlag, Berlin Heidelberg, pp. 156–162.
- Nath, B.N., Kunzendorf, H., Plüger, W.L., 2000. Influence of provenance, weathering, and sedimentary processes on the elemental ratios of the fine-grained fraction of the bedload sediments from the Vembanad Lake and the adjoining continental shelf, Southwest coast of India. *Journal of Sedimentary Research* 70 (5), 1081–1094.
- Nozaki, Y., Lerche, D., Alibo, D.S., Snidvongs, A., 2000. The estuarine geochemistry of rare earth elements and indium in the Chao Phraya River, Thailand. *Geochimica et Cosmochimica Acta* 64 (23), 3983–3994.
- Oliveira, S.M.B., Silva, P.S.C., Mazzilli, B.P., Favaro, D.I.T., Saueia, C.H., 2007. Rare earth elements as tracers of sediment contamination by phosphogypsum in the Santos estuary, southern Brazil. *Applied Geochemistry* 22 (4), 837–850.
- Park, B.K., Chang, S.K., Yoon, H.I., Chung, H., 1998. Recent retreat of the ice cliffs on King George Island, South Shetland Islands, Antarctic Peninsula. *Annals of Glaciology* 27, 633–635.
- Phedorin, M.A., Goldberg, E.L., Grachev, M.A., Levina, O.L., Khlystov, O.M., Dolbnya, I.P., 2000. The comparison of biogenic silica, Br and Nd distributions in the sediments of Lake Baikal as proxies of changing paleoclimates of the last 480 kyr. *Nuclear Instruments and Methods in Physics Research Section A* 448 (1–2), 400–406.
- Pichlmaier, M., Aquino, F.E., Silva, C.S., Braun, M., 2004. Suspended sediments in Admiralty Bay, King George Island (Antarctica). *Brazilian Antarctic Research* 4, 77–85.
- Santos, I.R., Silva-Filho, E.V., Schaefer, C.E., Albuquerque-Filho, M.R., Campos, L.S., 2005. Heavy metals contamination in coastal sediments and soils near the Brazilian Antarctic Station, King George Island. *Marine Pollution Bulletin* 50, 185–194.

- Santos, I.R., Silva-Filho, E.V., Schaefer, C.E., Sella, S.M., Silva, C.A., Gomes, V., Passos, M.J., Ngan, P.V., 2006. Baseline mercury and zinc concentrations in terrestrial and coastal organisms of Admiralty Bay, Antarctica. *Environmental Pollution* 140, 304–311.
- Schaefer, C.E., Francelino, M.R., Simas, F.N., Costa, L.M., 2004. Geologia e Geotectônica da Península Keller, Antártica marítima. In: Schaefer, C.E., Francelino, M.R., Simas, F.N., Albuquerque-Filho, M.R. (Eds.), *Ecosistemas costeiros e monitoramento ambiental da Antártica marítima, Baía do Almirantado, Ilha Rei George*. NEPUT, Viçosa, pp. 7–13.
- Simas, F.B., Schaefer, C.E., Melo, V.F., Guerra, M.B.B., Saunders, M., Gilkes, R.J., 2006. Clay-sized minerals in ornithogenic Cryosols from Admiralty Bay, King George Island, Antarctica. *Clays and Clay Minerals* 56, 723–738.
- Simões, J.C., Bremer, U.F., Aquino, F.E., Ferron, F.A., 1999. Morphology and variations of glacial drainage basins in the King George Island ice field, Antarctica. *Annals of Glaciology* 29, 220–224.
- Simões, J.C., Dani, N., Bremer, U.F., Aquino, F.E., Arigony-Neto, J., 2004. Small cirque glaciers retreat on Keller Peninsula, Admiralty Bay, King George Island, Antarctica. *Brazilian Antarctic Research* 4, 49–56.
- Smellie, J.L., Pankhurst, R.J., Thomson, M.R.A., Davies, R.E.S., 1984. The Geology the South Shetland Islands: VI. Stratigraphy, Geochemistry and Evolution, 87. *British Antarctic Survey Reports*. 83pp.
- Suguio, K., 1973. *Introdução a sedimentologia*. Edgard Blucher, São Paulo. 317 pp.
- Swarzenski, P.W., Baskaran, M., 2006. Uranium distribution in the coastal waters and pore waters of Tampa Bay, Florida. *Marine Chemistry* 102 (3–4), 252–266.
- Thomas, R., Rignot, E., Casassa, G., Kanagaratnam, P., Acuña, C., Akins, T., Brecher, H., Frederick, E., Gogineni, P., Krabill, W., Manizade, S., Ramamoorthy, H., Rivera, A., Russell, R., Sonntag, J., Swift, R., Yungel, J., Zwally, J., 2004. Accelerated sea-level rise from West Antarctica. *Science* 306, 255–258.
- Wasserman, J.C., Figueiredo, A.M.G., Pellegatti, F., Silva-Filho, E.V., 2001. Elemental composition of sediment cores from a mangrove environment using neutron activation analysis. *Journal of Geochemical Exploration* 72 (2), 129–146.
- Wedepohl, K.H., 1995. The composition of the continental crust. *Geochimica et Cosmochimica Acta* 59 (7), 1217–1232.
- Windom, H., Smith, R., Niencheski, F., Alexander, C., 2000. Uranium in rivers and estuaries of globally diverse, smaller watersheds. *Marine Chemistry* 68 (4), 307–321.
- Yang, S.Y., Lim, D.I., Jung, H.S., Oh, B.C., 2004. Geochemical composition and provenance discrimination of coastal sediments around Cheju Island in the southeastern Yellow Sea. *Marine Geology* 206 (1–4), 41–53.
- Yeo, J.P., Lee, J.I., Hur, S.D., Choi, B.G., 2004. Geochemistry of volcanic rocks in Barton and Weaver peninsulas, King George Island, Antarctica: implications for arc maturity and correlation with fossilized volcanic centers. *Geosciences Journal* 8 (1), 11–25.
- Yoon, H.I., Park, B.K., Kim, Y., Kim, D., 2000. Glaciomarine sedimentation and its paleoceanographic implications along the fjord margins in the South Shetland Islands, Antarctica during the last 6000 years. *Palaeogeography, Palaeoclimatology, Palaeoecology* 157 (3–4), 189–211.